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(54) Cementing compositions containing a copolymer as a fluid loss control additive.

(57) A cementing composition useful in cementing oil, gas and water wells, comprising water, hydraulic cement and an effective amount of water soluble fluid loss additive comprised of a copolymer of acrylamide/vinyl formamide and derivatives thereof in a weight percent ratio of from about 95:5 to 5:95, said copolymer having a molecular weight range of from about 100,000 to 3,000,000. The composition can also optionally include a dispersant such as sodium or potassium salts or a sulfonated naphthalene formaldehyde condensate.

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The present invention relates to an aqueous cementing composition containing a copolymer as a fluid loss additive. More particularly, the present invention relates to the cementing composition containing copolymer, prepared by the copolymerization of acrylamide and vinyl formamide in ratios of from about 95:5 to 5:95 by weight, as fluid loss additives.

The copolymerization of acrylamide and vinyl formamide with a suitable third monomer generally does not affect the effectiveness of these materials as fluid loss additives for cement slurries. Partial substitution of vinyl formamide with lower cost monomers which do not have deleterious effects on the stability of the polymer and rheology of the cement slurries can, in fact, be advantageously considered.

The incorporation of such copolymers and/or terpolymers as fluid loss additives for the cement slurries used in the completion of oil and gas wells, greatly reduces the loss of water from the cement slurry to the rock formation.

Optionally, a dispersant such as polynaphthalene sulfonate may also be incorporated into the cement slurry with the copolymer and/or terpolymer. When polynaphthalene sulfonate is incorporated into the slurry with the fluid loss additive, there is a synergistic effect between the dispersant and the additive which results in an even greater reduction of fluid loss than could be achieved using either ingredient alone.

The incorporation of the fluid loss additives of the present invention into cement slurries greatly reduces fluid loss in oil and gas well cementing operations and allows for a more efficient bonding between the oil or gas well liners and the rock formations.

Oil well cementing and other underground cementing operations often require placement of a slurry of cement, water and other additives in a porous environment such as porous earthen or rock strata. For example, cement compositions are routinely used in the oil and gas industry to cement the annular space in the well bore between the surrounding formation and the pipe or casing. Typically, the cement slurry is pumped down the inside of the casing and back up the outside of the casing through the annular space. The slurry is allowed to set up or harden in the annular space, thereby forming a rigid column which ideally forms a bond with the earth or rock formations as well as with the metal pipe or casing. To achieve a satisfactory primary cementing job, it is essential to achieve a tight bond to prevent vertical communication of fluids or gas along or within the column, which could contaminate the producing zone, or permit a loss of reserves.

The primary functions of the cementing process are to restrict fluid movement between geological formations and to bond and support the casing or metal pipe. In addition, the cement aids in protecting the casing from corrosion, preventing "blow-outs" by quickly sealing formations, protecting the casing from shock loads in drilling deeper wells and sealing off lost circulation or thief zones.

A common problem in petroleum well cementing is the flow of liquid from the slurry into the porous earth formations in contact with the cement. This fluid loss is undesirable since it causes thick filter cakes of cement solids which can ultimately plug the well bore. The fluid loss can also damage rock formations and affect well production. Fluid loss from cement slurries is particularly a problem in a process known as "squeeze cementing".

Problems develop when water filters out of the slurry and into the porous media during the placement and setting period of the cement. As a result of the attendant rapid water loss, the cement experiences impaired qualities of strength and an uncontrolled setting rate. Also, the water loss from the cement frequently damages the porous rock formations. This problem cannot be solved by adding more water to the slurry as this approach only exacerbates the problem. In addition, serious placing and setting problems may occur.

It is therefore of utmost importance that fluid loss control be achieved in order to insure satisfactory primary cementing. Inadequate fluid loss control can result in the formation of a bridge in the annulus opposite a permeable zone, thus isolating a lower zone from the hydrostatic pressure above the bridge. Only a small amount of filtrate loss beneath such a bridge is then necessary to drop the annular pressure to beneath that of the formation. The result is an influx of formation fluids and pressure, thereby creating flow channels and the need for often times expensive remedial work.

In order to attempt the control of fluid loss from the cement slurry to the surrounding rock formation, the cement matrix permeability must be reduced. This reduction allows the retention of a greater amount of water during the initial set, thereby effectively blocking the porous strata from the cement. The art is replete with examples of methods to achieve this goal. One way is to reduce filtrate mobility by increasing the filtrate viscosity to counter the normal thinning of the cement slurry which occurs at down hole temperatures. An increase in filtrate viscosity at down hole temperatures minimizes thermal thinning and increases the retention of the filtrate within the cement matrix. Conventional fluid loss additives do not satisfactorily address the problem of thermal thinning with increased temperature, thereby allowing increased fluid loss from the slurry to the formation and promotion of stratification of solids within the cement slurry column.

Accordingly, there is a greatly felt need for new materials which, when added to the cement slurries, reduce fluid loss to the surrounding rock formations.

Fluid loss additives in cementing compositions are old and well known in the art. Fluid loss additives have been discussed in the following articles:

Carter, Gregg and Slagle, Knox, "A Study of Completion Practices to Minimize Gas Communication", Society of Petroleum Engineers, Paper No. 3164, November 1970.

Christian, W.W., Chatterji, Jiten and Ostroot, Warren, "Gas Leakage in Primary Cementing - A Field Study and Laboratory Investigation", Society of Petroleum Engineers, Paper No. 5517, October, 1975.

Cook, C. Cunningham, W., "Filtrate Control: A Key in Successful Cementing Practices", Journal of Petroleum Technology, August, 1977, page 951.

Smith, Dwight, "Cementing: SPE Monograph Volume 4, published by Millet the Printer, Inc., Dallas, Texas, 1976.

The patent literature is also replete with many attempts to overcome the fluid loss control problems associated with oil and gas well cementing operations. There are many references directed to protecting potable water by isolating hydrocarbon bearing strata by efficient cementing operations.

U.S. 4,471,097 relates to auxiliary agents for chemical flooding of petroleum deposits and auxiliary agents used in well drilling fluids. These agents are water-soluble copolymers containing 20 to 80 percent by weight of unsaturated olefinic sulfonic acid, 5 to 15 percent by weight vinylacylamine, 0 to 40 percent by weight acrylamide and/or methacrylamide, 5 to 50 percent by weight vinylimidazole, 0 to 10 percent by weight of

$$CH_2 = \overset{R^5}{\overset{|}{C}}R^6$$

wherein R^5 is hydrogen or methyl, and R^6 represents hydroxy, alkoxycarbonyl with 1 to 12 carbon atoms in alkoxy moiety, cycloalkoxycarbonyl with 6 to 10 carbon atoms in cycloalkoxy moiety, phenyl, alkanoyloxy with 1 to 4 carbon atoms, or β-hydroxyalkoxycarbonyl with 2 or 3 carbon atoms in hydroxyalkoxy moiety; and 0 to 25 percent by weight of a cross-linking agent containing at least two olefinic double bonds.

These copolymers are used in drilling fluid additives during drilling operations. WP 8302449, which is the equivalent of U.S. 4,471,097 discloses the use of these copolymers in deep bore cement compositions to act as rheology additives.

No showing is made in Uhl et al of using these copolymers as fluid loss additives in cement slurries to avoid fluid loss from the cement to surrounding rock formations, and without adversely affecting the viscosity of the cement slurry.

U.S. 3,197,428 discloses

compositions comprising cement and copolymers of acrylamide and acrylic acid to improve well cementing operations and reduce fluid loss from the cement to the rock formations. However, the compositions of Siegle are not entirely satisfactory because they retard cement setting at high temperatures and so cannot be used at elevated temperatures and pressures such as are encountered in deep oil and gas well operations.

U.S. 3,359,225 discloses

cement additives containing polyvinylpyrrolidones and a condensate of sodium naphthalene sulfonate and formaldehyde. The polyvinylpyrrolidone reduces the separation of water from the cement slurry. The naphthalene sulfonate condensate is the dispersant. There is no teaching of the copolymers and/or terpolymers of the present invention.

U.S. 3,491,040 discloses

an aqueous hydraulic cement slurry including hydraulic cement, water, a surfactant and a small amount of polyalkylenepolyamine, polyalkenimine or mixtures thereof. Gibson et al also disclose a sulfonated naphthalene condensate dispersant as an additional additive to the cement slurry which cooperates with the polyamine additive to provide satisfactory fluid loss in cement slurries used at about 200°F and below. The sulfonated naphthalene dispersant is typically a low molecular weight material, e.g., in the range of about 1,000 to 3,000.

U.S. 3,409,080 discloses an

aqueous cementing composition which is adapted to high turbulent flow. The disclosure teaches the polyvinyl alcohol and polyvinyl acetate can be used as fluid loss additives in oil well cements.

U.S. 4,015,991
discloses a fluid loss additive for cement compositions which is a copolymer of acrylamide/2-acrylamido-2-methylpropane sulfonic acid derivative. These copolymers are useful only in operations where the bottom hole circulation temperature ranges from 90° to 125° F. Further, these copolymers have a salt tolerance of only up to 10 percent.

Cellulose-based fluid loss additives such as methyl cellulose, carboxymethylcellulose (CMC) and hydroxyethylcellulose (HEC) may be employed with or without a dispersant such as polynaphthalenesulfonic acid salts. However, there are several disadvantages to the use of CMC or HEC as cement fluid loss control additives. These materials are solid and as a result are difficult to handle in offshore operations. In addition, they tend to considerably increase slurry viscosity, thereby preventing its movement under turbulent flow conditions and retard the set of the cement. Also, these materials lose effectiveness in the presence of soluble calcium salts and at elevated temperatures.

The object of the invention is therefore to provide a cementing composition containing a fluid loss additive that has as little effect on cement properties as is possible and still provides for the fluid loss properties which are necessary for the cementing of casings to rock formations. Further, any fluid loss additives should be compatible with as many other additives as possible and should be usable over as wide a range of temperatures and other environmental conditions as is possible.

The present invention relates to cementing compositions and more particularly to fluid loss additives which may be incorporated into the cement compositions. The cement compositions are useful in cementing operations in oil and gas wells and are comprised of water, hydraulic cement and copolymers and/or terpolymers. When a copolymer of acrylamide and vinyl formamide is used, the monomers are present in a ratio of 95:5 to 5:95, and more preferably in a ratio of from about 80:20 to 20:80. When a terpolymer is to be used, it may consist of acrylamide and vinyl formamide and any other suitable monomer. The terpolymer is comprised of 5 to 95 to 95 to 5 weight percent of acrylamide and vinyl formamide, and 0 to 60 weight percent additional monomer. The copolymer has a molecular weight range of from about 10,000 to 3,000,000 and preferably between 100,000 to 1,000,000 where the molecular weights have been determined by GPC using polyethylene glycol standards. When a terpolymer is employed, it has a molecular weight range of from about 10,000 to 3,000,000, and preferably between 100,000 to 1,000,000. The copolymer and/or terpolymer function as fluid loss additives and are present in an amount effective to reduce fluid loss from the cement slurry to surrounding rock formations.

Optionally, the cementing composition may contain an effective amount of a dispersant such as polynaphthalene sulfonate. When this dispersant is present, there is a synergistic effect between the dispersant and the fluid loss additive which results in greater effectiveness of the system in reducing fluid loss than could be expected when using the dispersant and copolymer and/or terpolymer separately. The dispersant also further decreases the viscosity of the slurry, thereby aiding in pumping of the slurry into the annular space.

The fluid loss additive may be used in any amount which is effective in reducing the fluid loss from the cement slurry to the surrounding rock formations. Ideally, the fluid loss additive should be present in an amount of about 0.05 to 2.0 percent by weight of the cement, and preferably in an amount of about 0.125 to 1.0 percent by weight of the cement.

Cementing compositions are disclosed which provide for fluid loss control and use over a wide range of temperature and well conditions. The cementing compositions are comprised of water, hydraulic cement, a fluid loss additive comprising a particular copolymer of an acrylamide type monomer and a basic monomer such as vinylformamide, its hydrolysis products and derivatives hereof, or a terpolymer of acrylamide, vinyl formamide and any other suitable monomer, and optionally, a dispersant such as polynaphthalene sulfonate. The use of a dispersant has a synergistic effect on the copolymer or terpolymer and results in an unexpected increase in its effectiveness as a fluid loss additive.

The copolymer used in the cementing compositions of this invention include an acrylamide and associated acrylamide derivatives selected from the group consisting of acrylamide, methacrylamide, N,N, dimethyl(meth)acrylamide, N,N, dialkylamino- alkyl(meth)acrylamide, and mixtures thereof. The other monomer of the acrylamide/vinyl formamide copolymer is vinyl formamide, its hydrolysis products and derivatives thereof. These are copolymerized in a weight ratio of from about 95:5 to 5:95 and preferably 80:20 to 20:80. The copolymer has a molecular weight of from about 10,000 to 3,000,000 and preferably between 100,000 to 1,000,000.

The copolymer is made in a conventional copolymerization process such as solution, emulsion or bulk polymerization in the presence of conventional free radical initiators. Such procedures are well documented and are well known to those skilled in the art.

The terpolymer may include any suitable monomer in addition to the copolymer mentioned above.

These monomers may include unsaturated acid monomers and alkali metal, ammonium or organic amine salts thereof, water soluble or dispersible derivatives of acrylic acid and acrylamide such as N,N-dialkylaminoalkyl(meth)acrylamide, N,N-dialkylaminoalkyl(meth)acrylate, ethyl acrylate, methyl acrylate, acrylamido methylpropane sulfonic acid sodium salt, hydroxypropylacrylate and other vinyl monomers with sufficient water solubility or dispersibility such as vinyl pyrrolidone, sodium vinylsulfonate, acrylonitrile, vinylacetate. The quaternary salts of the appropriate amino containing monomers listed above are also suitable comonomers for the terpolymers in question.

In its terpolymer form, the range of the three components is from about 0 to 60 weight percent additional monomer, from about 5 to 95 weight percent acrylamide and from about 5 to 95 weight percent vinyl formamide.

The terpolymers are made by conventional polymerization techniques as are well known to those skilled in the art.

The polymers can be added to the cement composition in dry, solution or emulsion form.

The result of the inclusion of the fluid loss additives of the present invention are improved pumpability of the cement which generally improves drilling fluid removal and reduced possibility of lost circulation, when cementing a conduit penetrating a permeable earthen formation.

The cement component of the cement composition of this invention may be any of the API classes of cement or cement blends, as are defined in the American Petroleum Institute Bulletin entitled "API Specification for Material and Testing for Well Cements", Third Edition, dated July 1, 1986 ("API Spec. 10"), and incorporated herein by reference. These include cements defined as Classes A through H in API Spec. 10.

As previously stated, the cement compositions of this invention may optionally include dispersants such as any anionic surfactant i.e., any compound which contains a hydrophobic portion (e.g., any hydrocarbon substituent such as alkyl, aryl or alkylaryl group) and a hydrophilic portion (e.g., any negatively charged moiety, such as O^-, $CO^-{}_2$, or $SO^-{}_3$). Suitable dispersants include sulfonic acid derivatives of aromatic hydrocarbons, such as naphthalene sulfonic acid formaldehyde condensation product derivatives, particularly their sodium or potassium salts. Examples of dispersants which may be used include lignosulfonates, sodium and potassium naphthalene sulfonate formaldehyde condensation products (such as LOMAR D commercially available from Diamond Shamrock Chemical Company), and sodium salts of ketone sulfonate formaldehyde.

The cement compositions may also include at least one inorganic salt. Suitable salts include inorganic monovalent and polyvalent metal salts, such as magnesium chloride, ammonium chloride, sodium and potassium chloride and calcium chloride.

Other additives conventionally added to cement compositions useful in cementing casings in the bore hole of a well can also be added to the cement compositions of this invention in the amount which are normally used by those skilled in the art. These additives may include, for example, (1) heavy weight additives, such as hematite, ilmenite, silica flour and sand; (2) cement retarders such as lignins and lignosulfonates; and (3) additives for controlling lost circulation; such as walnut hulls and cellophane flakes.

The fluid loss additives of the present invention will effect a substantial reduction in the rate of water loss by filtration and in the apparent viscosity of the cement slurries. They are easily mixable and result in good fluid loss control while still exhibiting good flow properties at 0.05 percent to 2 percent by weight addition to the cement, depending upon the type of cement. Under API standards, excellent fluid loss rates below 100 cc/30 min can be achieved by the addition of about 0.05 percent to 2 percent by weight of the cement of such fluid loss additive to cement slurry of average density. Typically, a fluid loss of between about 20 and 100 cc/30 min., can be observed with a 0.25 percent to 0.50 percent by weight of the cement (BWOC) addition of the additives of the present invention.

Fluid loss properties can be controlled in salt cement formulations (such as up to saturated NaCl and seawater) with the addition of 0.25 percent to 0.50 percent by weight of the cement of the additives of the present invention without affecting rheology adversely.

The polymeric additives of the present invention exhibit some retardation effects on the cement slurry. The magnitude of the increase in thickening time of the cement slurries will depend on the temperature, pressures and slurry composition. Also, the additives of the present invention do not excessively thicken the cement, which allows for the incorporation into the cement of other additives and ingredients as may be dictated by on-site use conditions.

The following examples are presented in order to illustrate various aspects of the invention.

In the following Examples, all cement slurries were prepared according to API Spec. 10, Third Edition, July 1, 1986.

Table I is an explanation of the symbols and abbreviations used in the table containing the data of the

examples. The symbols and abbreviations used therein are standard in the art and are well known to those of ordinary skill in the art.

Table II indicates the copolymer works quite well as a fluid loss additive at 60° and 82° C and works well at 37.8° C when it is partially hydrolyzed with caustic solution.

Table I

SYMBOLS USED IN TABLES

% Additive	(g. additive/g. cement)x100
% LomarD	(g. LomarD/g. cement)x100
Lomar D	Sodium sulfonated naphthalene/ formaldehyde condensate from Diamond Shamrock (Henkel)
PV	Plastic Viscosity - cP (mPa.s)
FL	mL. of cement filtrate through a 325 mesh (45 µm) stainless steel screen @ 1000 psi ΔP
FW	mL. of supernatant liquid above a column of cement slurry in a stoppered 250-mL. graduated cylinder after 2 hours @ ambient temperature.
RTSet	Sample left overnight at room temperature hardened to a competent mass.
NS	Not set overnight at room temperature.
TT	Time in minutes to reach 70 Bc (Bearden Units of Consistency). 100 Bc - 1000 mPa.S.
CS	Compressive strength in psi after 24 hours

Table II

PERFORMANCE OF AN ACRYLAMIDE/VINYLFORMAMIDE (AM/VFA) COPOLYMER AS A FLUID LOSS CONTROL ADDITIVE FOR OIL WELL CEMENTING CLASS H CEMENT, 38% H_2O

API TESTS, 1000 psi[2]

AM/VFA 75/25

Example No.	% Additive	% LomarD	FL(mL)	FW(mL)	PV	TT(min)[1]	CS(psi)[2]
			37.8°C				
1**	0.50	0.50	25		81	--	--
			60°C				
2	0.25	0.50	61	1.0	--	--	--
			82°C				
3	0.0	0.0	1628	--	--	105	5000
4	0.25	0.50	129	1.0	90	--	
5	0.25	0.75	106	1.0	81	>300	
	0.25	0.75	--	--	--	326[3]	
6	0.25	1.00	48	1.0	86	>450	4336
7	0.35	0.50	94	0.1	99	>420	4232
8	0.50	0.50	44	0.1	126	>450	SetRT
9	0.50	0.75	28	0.1	144	>450	NS
10	0.50	1.00	28	0.1	204	>450	1196

** A sample of Am/VFA was mixed with a 50% NaOH solution, heated to 82°C for 1 hour, allowed to cool then used in Example 4.

1) Thickening times were under atmospheric pressure, unless otherwise noted.
2) 24 hour cure time at 82°C and 3000 psi
3) This test using API schedule 6g7 for a 10,000 ft (3040 m.) well.

Claims

1. A cementing composition useful in cementing oil, gas and water wells comprising:
   a) water;
   b) hydraulic cement; and
   c) a fluid loss additive in small amounts, said fluid loss additive comprised
   of a copolymer of acrylamide and vinyl formamide and derivatives thereof in a weight percent ratio of from about 95:5 to 5:95, said copolymer having a molecular weight range of from about 10,000 to 3,000,000, said acrylamide monomer selected from the group consisting of acrylamide, methacrylamide, N,N-dimethyl(meth)acrylamide, dialkylaminoalkyl(meth) acrylamide and mixtures thereof, said vinyl selected from the group vinylformamide, its hydrolysis products and derivatives thereof.

2. The composition of claim 1, wherein the fluid loss additive is present in an amount of from about 0.05 to 2.0 percent by weight of the cement.

3. The composition of claim 1, wherein the copolymer has a molecular weight of from about 100,000 to 1,000,000.

4. The composition of claim 1, further including a synergistic amount of a dispersant selected from the group consisting of lignosulfonates, sodium or potassium salts of a sulfonated naphthalene formaldehyde condensate, sodium salts of ketone sulfonate formaldehyde condensate, and mixtures thereof.

5. The composition of claim 1, wherein the copolymer is comprised of a 80:20 to 20:80 weight percent ratio of acrylamide to vinylformamide.

6. The composition of claim 1, wherein the copolymer is polymerized with another monomer to create an acrylamide/vinylformamide/monomer terpolymer having an average molecular weight range of from about 10,000 to 3,000,000.

7. The composition of claim 6, wherein the monomer is selected from the group consisting of unsaturated acid monomers, alkali metals, ammonium, ammonium organic amine salts, N,H-dialkylaminoalkyl(meth)-acrylamide, N,N-dialkylaminoalkyl(meth)acrylate, ethylacrylate, methyl acrylate, acrylamido methyl-propane sulfonic acid sodium salt, hydroxy-propyl-acrylate, vinylpyrrolidone, sodium vinylsulfonate, acrylonitrile, vinylacetate and quaternary salts of the amino groups containing monomers, and mixtures thereof.

8. The composition of claim 6, wherein said terpolymer is comprised of from about 0 to 60 weight percent additional monomer, from about 5 to 95 weight percent acrylamide and from about 5 to 95 weight percent vinylformamide.

9. Use of a copolymer of acrylamide and vinyl formamide and derivatives thereof in a weight percent ratio of from about 95:5 to 5:95, said copolymer having a molecular weight range of from about 10,000 to 3,000,000, said acrylamide monomer selected from the group consisting of acrylamide, methacrylamide, N,N-dimethyl(meth)acrylamide, dialkylaminoalkyl(meth) acrylamide, dialkylaminoalkyl-(meth)acrylamide and mixtures thereof, said vinyl selected from the group vinylformamide, its hydrolysis products and derivatives thereof, in small amounts as a fluid loss additive in water and hydraulic cement containing cementing compositions.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 2217

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 331 045 (AIR PRODUCTS CHEMICALS) * Claim 1; page 5, lines 49-56; page 4, lines 5-6 * – – –	1-5,9	E 21 B 33/13 C 04 B 24/26
X	EP-A-0 342 500 (BASF) * Claims 1-4,6-16 * – – –	6-8	
X	EP-A-0 196 689 (DOWELL SCHLUMBERGER) * Claims 1,2,6; page 5, paragraphs 3-8 * – – – – –	6-8	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)
E 21 B C 04 B

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	24 May 91	ROTSAERT L.D.C.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention

E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document